Evaluation of Ambient Non-Methane Hydrocarbon Measurements Taken During the Winter of 1991-92 in Sacramento, California

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ABSTRACT

The 1991-92 Sacramento Area Winter Hydrocarbon Study was undertaken by the California Air Resources Board (CARB) to examine the nature and distribution of ambient non-methane hydrocarbon (NMHC) species with respect to their concentrations and profiles. The winter period was selected as a time when hydrocarbon emissions would be least affected by photochemistry and afternoon mixing, and stable conditions would permit an examination of the impact of local emissions sources on air monitoring stations. The Study included measurements of speciated and total hydrocarbon measurements from four fixed monitoring sites and six mobile sites during the morning and afternoon. The evaluation of these results is intended to help develop a better understanding of the local and regional distribution of hydrocarbons in the Sacramento area, with a particular emphasis on specific hydrocarbon patterns in urbanized areas. In addition to examining spatial distribution, the paper contains an evaluation of a temporal (morning vs. afternoon) NMHC species, and a brief comparison to similar data collected during the ozone season.

Ultimately, the spatial and temporal information from the Sacramento Winter Study and other monitoring programs will benefit ozone assessment activities and regulatory efforts. The United States Environmental Protection Agency (US-EPA) will be requiring extensive routine collection of VOC samples as part of the Photochemical Assessment Monitoring Station (PAMS) network in California. CARB and other state and local air pollution control agencies are exploring alternative collection schedules that will meet the PAMS data uses. The results of this and other intensive studies are an appropriate basis from which to develop the first years of the required network plans, particularly to meet those aspects that require a general characterization of precursor behavior.

INTRODUCTION

Intensive air quality studies began in California in 1985 to collect complex aerometric data in support of photochemical ozone models. The information was used in part to verify and evaluate model performance and usage. Since 1985, each major urban area in

California has participated in a similar intensive data collection program. The Monitoring and Laboratory Division (MLD) of the California Air Resources Board began a routine seasonal sampling program in 1989 to gather information about NMHC species in the high ozone areas of the state. The emphasis of most of the above studies has been to characterize precursor behavior on summer days.

Recently, new uses of detailed aerometric data have been identified that address air quality issues with a broader view. The Southern California Air Quality Study (SCAQS) and CARB's own summer hydrocarbon studies have helped illustrate the varied uses of non-methane hydrocarbon data. [1] For example, NMHC data were useful in ARB's recent "top down" review of the emission inventory. [2] In addition, the SCAQS study revealed NMHC concentrations in the fall/winter period were generally twice as high as those observed during the summer. The SCAQS data also indicated the presence of a clear bimodal diurnal NMHC profile, a feature that is often obscured on hot summer afternoons and most probably caused by photochemical reaction or increased mixing. Winter studies also were a specific recommendation of the National Academy of Science/National Research Council in its report "Rethinking the Ozone Problem." [3]

To augment existing information, the CARB-MLD, with the assistance of the Sacramento Metropolitan Air Quality Management District, designed the Winter Study to examine the nature of sources, reactivity, and diurnal patterns of ambient hydrocarbon levels. The Sacramento area was selected because winter meteorology in the region is often stable with limited ventilation and mixing. The area was also selected because recent summer NMHC data would be available for comparison, and the sites were located near the CARB-MLD laboratory facilities. Because Sacramento has been identified by US-EPA as requiring Federal Clean Air Act-mandated "enhanced ozone" monitoring, the information from the Winter Study could help determine the need for future NMHC monitoring to characterize and track changes to ozone precursors over time.

DESCRIPTION OF STUDY

The Winter Study data collection occurred during the period of December 1991 through February 1992. The data were evaluated to determine whether the NMHC profiles and patterns were consistent throughout the urbanized area. For purposes of this paper, the term NMHC is used to refer to C2-C10 hydrocarbon compounds. The study results also include an assessment of the temporal NMHC sampling for the morning and afternoon of each sampling results.

Monitoring Site Selection

The hydrocarbon samples at the fixed locations were collected at four State and Local Air Monitoring Station (SLAMS) sites. They were:

1) The CARB-MLD downtown site at 13th and T Street. This site was selected as representing the Central Business District (CBD), an area characteristic of maximum ozone precursor emissions,

2) Two sites, Del Paso Manor and North Highlands, represent the fringe of the CBD, an area just downwind of maximum precursor emissions; and,

3) A downwind site in Rocklin approximately 13 miles northeast of the CBD in Placer County. The Rocklin site is representative of an area of high ozone concentrations in the summer.

In addition to total and speciated NMHC information, each site was equipped with ozone, nitrogen oxides, carbon monoxide, and meteorological analyzers or sensors. A map of the study area is included in Figure 1.

Intensive spatial sampling was also conducted. The first of these two components of the Study was an investigation of the representativeness of the CARB-MLD site within the CBD. A mobile air monitoring station with hydrocarbon and meteorological sampling capabilities was employed at two locations equally spaced within the CBD. The mobile site was later moved to two point sources, McClellan Air Force Base and an industrial site, to gather information regarding air monitoring site placement and the role siting has on tracking NMHC emissions from large sources. This paper contains a brief discussion of the data related to the point sources. A complete analysis of that element of the program is not within the scope of this paper.

Conventional Sampling and Analysis Methods Employed for NMHC Monitoring

Whole air samples were collected in six-liter stainless steel canisters. Samples were taken between 6-9 AM and 1-4 PM on a one-in-three-day schedule. Samples were collected using a Xontech 910a/912 sampler developed for the CARB-MLD toxic sampling program. The samplers are programmable and samples were retrieved by the technician every six days. The MLD-Northern Laboratory Branch pre-concentrated the samples and analyzed them by use of a gas chromatograph (GC) equipped with a flame ionization detector. Speciated results were generated using a separation column. Total NMHC results were generated by a GC without a separation column by the method known as pre-concentration direct flame ionization detection (PDFID).

HYDROCARBON DATA

Continuous Measurement of Total Non-Methane Hydrocarbons

A continuous NMHC monitor (modified CE 8202) was used throughout the duration of the Winter Study at the CARB-MLD site at 13th & T Street. The continuous analyzer had been modified to increase its sensitivity to improve performance. The average of the three hourly average NMHC values compared favorably to the integrated samples collected by the canister-laboratory. Although the laboratory generated data is generally accepted to have greater accuracy and precision, the continuous analyzer provides around-the-clock information at a fraction of the cost of a canister based program. Currently,

CARB-MLD is assisting in the development of an improved continuous total NMHC monitor capable of direct NMHC measurements.

PDFID Measurements of Non-Methane Hydrocarbons

A total of fifty canister samples were collected at the six mobile sites. As indicated earlier, two mobile sites were located within the CBD to examine the representativeness of the fixed monitoring station at 13th and T Street. A comparison of total NMHC for the three CBD sites is shown in Figure 2. In general, NMHC concentrations at the mobile sites at 20th & L Street and City Hall were similar to concentrations observed at the 13th & T Street fixed site. One exception occurred during the afternoon at the 20th & L site; however, with the exception of a modest increase in C2s, the profile of NMHC species was largely the same as on the succeeding and other days. These results tend to validate the 13th & T Street site as a representative CBD monitoring site.

Total NMHC concentrations for the four fixed SLAMS sites are illustrated in Figure 3. As can be seen, NMHC concentrations vary somewhat day-to-day and morning to afternoon. On many of the days, the data from CBD confirmed the site as representing a "maximum emission" site type. On other days, however, NMHC concentrations from the four sites were rather similar. Average NMHC concentrations at the three fixed sites outside the CBD, Del Paso, North Highlands, and Rocklin, were similar, with Rocklin, the site intended to represent the downwind, maximum ozone site, tending to be lower. Morning average NMHC concentrations were generally 50 to 100 percent larger than levels seen in the afternoon.

Speciated Data

During the three-month sampling period of the Winter Study, 258 canister samples were collected and analyzed for 94 hydrocarbon species. Typically, the concentration of two-thirds of the species measured fell below detectable levels of 0.1 pphm-C. Species rarely detected typically yielded average values near the limit of detection (LOD). As is often observed, the variability of the measurement decreased with increasing concentration. For purposes of our assessment, a sub-set of 32 well represented target species was used each having 50 percent or more of the individual values above the LOD. A list of the 32 compounds and their average mass values for the 13th & T Street site is presented in Table 1.

EVALUATION OF SPECIATED HYDROCARBON PROFILES OF SACRAMENTO WINTER

Morning vs. Afternoon

One goal of the Winter Study was to investigate the temporal distribution of NMHC within the Sacramento region. The comparison between the morning and afternoon samples has already indicated a difference in total NMHC mass; however, a distinct pattern emerged upon evaluation of the profile of normalized species concentrations.

Normalizing was performed on each sample simply by dividing the concentration of target compound by the total NMHC concentration as determined by the PDFID method.

The normalized average for each target species at each fixed site was calculated among samples taken at identical times of the day (morning or afternoon). The results are displayed graphically in Figures 4 through 7. The similarity of morning vs. the afternoon profiles for all target compounds can be readily seen in the four figures as can the similarity in the profiles between sites. Table II contains a site-by-site summary of the normalized species profile. As was observed in the SCAQS study, the data appears to indicate a uniform and consistent emission profile throughout the region. These results suggest that tracking changes to emission patterns could be performed using suitable representative sampling.

An assessment of the variability of the normalized mean was performed by combining morning and afternoon samples. The 95 percent confidence interval of the mean percent fraction was calculated for each species at each fixed site. The results of these calculations are graphically represented in Figure 8 for the 13th & T Street site. The narrow separation of the upper and lower confidence bands suggest the normalized mean is well defined and supports the notion of a distinguishable profile for hydrocarbon species.

Inter-Comparison of the Four Fixed Sacramento Sites and Mobile Sites

The mobile station was deployed at two presumably source-dominant locations. The facilities were among the largest sources of NMHC in the region and were located in areas of mixed land uses. A distinctive NMHC signature that could be attributed to the facility was derived from information supplied by one facility about its processes and from grab samples taken from the stacks. The mobile site was situated at two locations at each facility to improve the chances of the plume contacting the monitoring site. A source signature was considered evident if a change in the target species occurred at either site around the facility. The mobile station was located at each site for two weeks. The special study areas, including the downtown area, are shown in Figure 1.

The profiles of the normalized target species from both fixed and mobile sites are summarized in Table II. For most species, the averaged normalized differences tended to be small with the possible exception of elevated levels of propene, hexane, methylcyclohexane, and toluene at the mobile sites located in the vicinity of the industrial site. Some of the elevated constituents were consistent with the source's signature. Detection of the source signature, however, was not observed at any of the other fixed sites. This preliminary view suggests that within the Sacramento area, the ambient NMHC mix is frequently repeated with slight differences observed in close proximity to high emission sources. A more complete assessment using samplers spaced at different distances from the sources would be helpful in determining acceptable siting requirements if one wished to track changes in emissions from large stationary sources.

SUMMER VS. WINTER TRENDS

A direct comparison of winter to summer species profiles was possible using morning (6-9 am) samples collected at the CARB-MLD site at 13th & T Street. Figure 9 depicts the 32 NMHC species that represent the summer of 1991, normalized in the same manner as was done for the winter data. For most species, the differences of the averaged normalized values were small with the most notable differences occurring with ethene/ethyne (co-elution) and butane and 2-methyl butane. Variation in the former species pair, while more pronounced between summer and winter, was evident within the winter data set. The difference between the butane fractions is likely accounted for by the change in the gasoline formulation (lowering the Reid vapor pressure in summer) between two seasons.

The differences noted between summer and winter at 13th and T Street in Sacramento are generally repeated in a subsequent comparison of an average morning Winter Study profile to average morning species observed at all 7 summer sites in the CARB-MLD summer monitoring program, i.e. Sacramento, San Diego, Los Angeles, Bakersfield, Modesto, Stockton, and Fremont. The results are displayed in Figure 10. These results suggest a strong similarity in average ambient hydrocarbon profiles in California.

CONCLUSIONS

Winter studies in California can be useful tools for understanding hydrocarbon emissions given that photochemical reactions that affect hydrocarbon species are reduced and there is a greater occurrence of stable meteorological conditions. This Study revealed that the ambient NMHC profiles between summer and winter in the Sacramento area were largely similar. The similarity extends both spatially and temporally in winter NMHC profiles within the Sacramento region. In addition, specific sites within the Sacramento CBD did not yield significantly different total NMHC concentrations or species profiles.

The similarity in NMHC species distribution should enable areas in California to meet the PAMS objectives relating to trends and characterizing an area's NMHC profiles with a schedule of periodic sampling. Data from routine total NMHC samplers could be considered in some areas to supplement periodic speciated sampling to meet many of the PAMS objectives once the species pattern(s) has been established. The needs of modelers may require more intensive precursor sampling on ozone episode days, at least initially. More work is needed to investigate siting requirements to track emissions changes of stationary sources, particularly in the area of solvent usage.

ACKNOWLEDGMENTS

The Sacramento Area Winter Study was sponsored by the Monitoring and Laboratory Division of the CARB under the general supervision of William Loscutoff, Division Chief. Two of the four fixed monitoring stations and all mobile stations were operated and maintained by Bill Oslund and his staff of the Air Quality Surveillance Branch (AQSB) of MLD. The AQSB was also responsible for the operation and direct comparison of the

performance of various analyzers at 13th and T Street. Michael Poore and his staff of the Northern Laboratory Branch of MLD analyzed all the canister samples for both total and speciated NMHC. George Lew and his staff of the Engineering Evaluation Branch provided the source test and facility process information. The staff of the Quality Management and Operations Support Branch provided general guidance on the Study design, data analyses, quality assurance, and mobile site sample collection. The Sacramento Metropolitan Air Quality Management District maintained two of the four fixed air monitoring stations. In addition, the authors wish to express their appreciation to Karen Hawk for her preparation of the tables and graphs for this paper.

REFERENCES

1. California Air Resources Board, Analysis of the Ambient VOC Data Collected in the Southern California Air Quality Study, contract number A832-130 final report from Sonoma Technology, Feb. 1992.

2. Fujita, E.M., B.E. Croes, C.L. Bennett, D.R. Lawson, F.W. Lurmann, H.H. Main, "Comparison of Emission Inventory and Ambient Concentration Ratios of CO, NMOG, and NOx in California's South Coast Air Basin," Journal of Air & Waste Management Association, 42(3): 264-276, March 1992.

3. National Research Council, Rethinking the Ozone Problem in Urban and Regional Air Pollution, National Academy Press, Washington, D.C. 1991

Table I. 32 Compounds With At Least 50% Data Completeness At Sacramento (13th & T)

	Compound	Average mass (pphm-C)
*	Ethene/Ethyne	2.85
	Ethane	0.96
	Propene	0.58
	Propane	1.73
	Methylpropane	0.99
*	Methylpropene/1-Butene	0.52
	Butane	2.43
	2-Methylbutane	2.25
	Pentane	0.79
	2,3-Dimethylbutane	0.17
	2-Methylpentane	0.69
	3-Methylpentane	0.42
	Hexane	0.35
	Methylcyclopentane	0.45
	Benzene	1.06
	2-Methylhexane	0.24
	3-Methylhexane	0.26
	2,2,4-Trimethpentane	0.32
	Heptane	0.18
	Methylcyclohexane	0.23
	Toluene	2.17
	3-Ethylhexane	0.15
	Ethylbenzene	0.41
*	m/p-Xylene	1.35
	o-Xylene	0.51
	1-Methyl, 3-ethylbenzene	0.33
	1-Methyl, 4-ethylbenzene	0.15
	1,2,4-Trimethylbenzene	0.50
	1,2,3-Trimethylbenzene	0.19

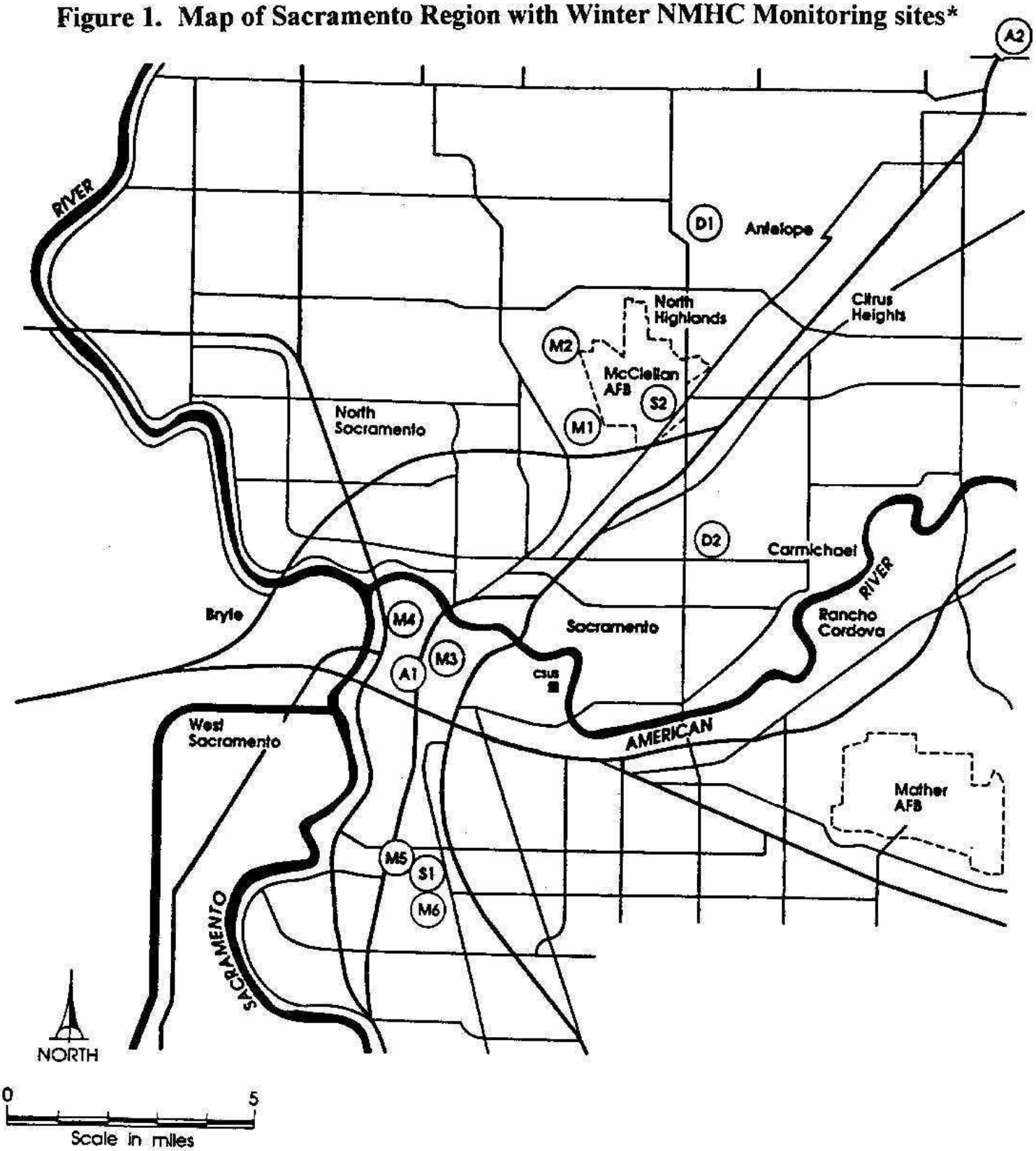
* Two compounds unseparated in the speciate analysis.

Table II. Summary of Average Percent Fraction for Individual Species with respect to Total NMHC

	Fixed Air Monitoring Sites					Mobile Air Monitoring Sites					
Representative Area*	CBD	FCBD	FCBD	DW		CBD		Industrial Site		McClellan AFB	
	13th & T	Del Paso	No. High.	Rocklin	**AVG**	20th & L	City Hall	Storage	47th	Bell	Ascot
Ethene/Ethyne	7.7	8.5	7.1	7.8	**7.8**	7.4	8.6	7.2	6.6	10.0	8.2
Ethane	2.9	3.0	2.9	2.9	**2.9**	2.1	3.2	2.5	1.8	2.6	3.2
Propene	1.5	1.6	1.3	1.7	**1.5**	1.9	1.5	1.5	2.3	2.1	2.0
Propane	5.4	5.4	4.9	6.2	**5.5**	6.2	6.6	4.0	5.3	4.2	6.3
Methylpropane	2.8	2.6	2.7	2.6	**2.7**	2.3	2.9	3.0	2.6	1.7	2.3
Methylpropene/1-Butene	1.6	2.0	1.2	1.2	**1.5**	1.4	1.0	1.5	1.1	1.2	3.4
Butane	6.9	6.2	7.1	7.0	**6.8**	6.8	6.8	6.4	5.8	7.0	6.9
2-Methylbutane	6.4	5.7	6.1	5.5	**5.9**	5.9	6.0	6.3	6.1	7.1	6.0
Pentane	2.3	2.1	2.1	2.0	**2.1**	2.1	2.3	2.1	2.1	2.4	1.9
2,3-Dimethylbutane	0.4	0.5	0.5	0.5	**0.5**	0.5	0.5	0.5	0.5	0.5	0.6
2-Methylpentane	1.9	1.9	1.9	1.8	**1.9**	2.0	2.0	1.9	2.2	2.3	1.7
3-Methylpentane	1.2	1.1	1.1	1.0	**1.1**	1.2	1.3	1.1	1.4	1.4	1.0
Hexane	0.9	0.9	0.9	0.9	**0.9**	1.3	1.1	1.0	1.8	1.3	0.9
Methylcyclopentane	1.2	1.1	1.2	1.0	**1.1**	1.3	1.4	1.1	1.5	1.5	1.2
Benzene	3.0	3.1	2.9	3.1	**3.0**	3.1	3.2	2.7	2.8	3.8	2.9
2-Methylhexane	0.6	0.7	0.6	0.6	**0.6**	0.8	0.8	0.6	0.8	1.0	0.8
3-Methylhexane	0.7	0.7	0.7	0.6	**0.7**	0.7	0.7	0.7	0.9	0.8	0.7
2,2,4-Trimethpentane	0.8	0.8	1.1	0.8	**0.9**	0.8	0.8	0.7	0.9	1.1	1.0
Heptane	0.5	0.5	0.5	0.6	**0.5**	0.4	0.5	0.5	0.8	0.6	0.6
Methylcyclohexane	0.6	0.6	0.6	0.7	**0.6**	0.5	0.7	0.7	1.5	0.6	0.6
Toluene	6.0	5.7	6.1	5.2	**5.8**	6.6	6.0	10.1	8.6	7.3	5.5
3-Ethylhexane	0.6	0.8	0.6	0.8	**0.7**	0.4	0.3	0.6	0.5	0.5	0.7
Ethylbenzene	1.1	1.1	1.1	1.0	**1.1**	1.2	1.1	1.0	1.4	1.4	1.0
m/p-Xylene	3.7	3.7	3.7	3.4	**3.6**	4.1	3.7	3.6	4.7	4.5	3.2
o-Xylene	1.4	1.4	1.4	1.3	**1.4**	1.6	1.4	1.4	1.8	1.7	1.3
1-Methyl, 3-ethylbenzene	0.8	0.8	0.8	0.8	**0.8**	1.0	1.0	0.9	1.0	1.0	0.9
1-Methyl, 4-ethylbenzene	0.4	0.5	0.4	0.4	**0.4**	0.4	0.5	0.4	0.4	0.4	0.5
1,2,4-Trimethylbenzene	1.4	1.4	1.3	1.3	**1.3**	1.5	1.4	1.4	1.6	1.6	1.3
1,2,3-Trimethylbenzene	0.6	0.7	0.6	0.9	**0.7**	0.5	0.5	0.7	0.5	1.1	0.7

*CBD-Central Business District, FCBD-Fringe CBD, DW-Down Wind of CBD

Figure 1. Map of Sacramento Region with Winter NMHC Monitoring sites*



*A1	CARB Laboratory Office - 13th &T Streets	M1	Mobile Station - Bell Ave. Fire Station
A2	CARB Rocklin Station	M2	Mobile Station - Army Corp. of Eng. - Ascot Ave.
D1	District - North Highlands Station	M3	Mobile Station - 2020 L Street (CARB Hdqtrs.)
D2	District - Del Paso Manor Sacramento Station	M4	Mobile Station - Sacto. City Hall (10th &H Sts.)
S1	Source - Industry	M5	Mobile Station - Sacto. City Storage Yard
S2	Source - McClellan AFB	M6	Mobile Station - ABF Freight 3240 47th Ave.

Figure 2. Total NMHC for Sacramento-13th & T and 2 Mobile Sites (Winter 91-92)

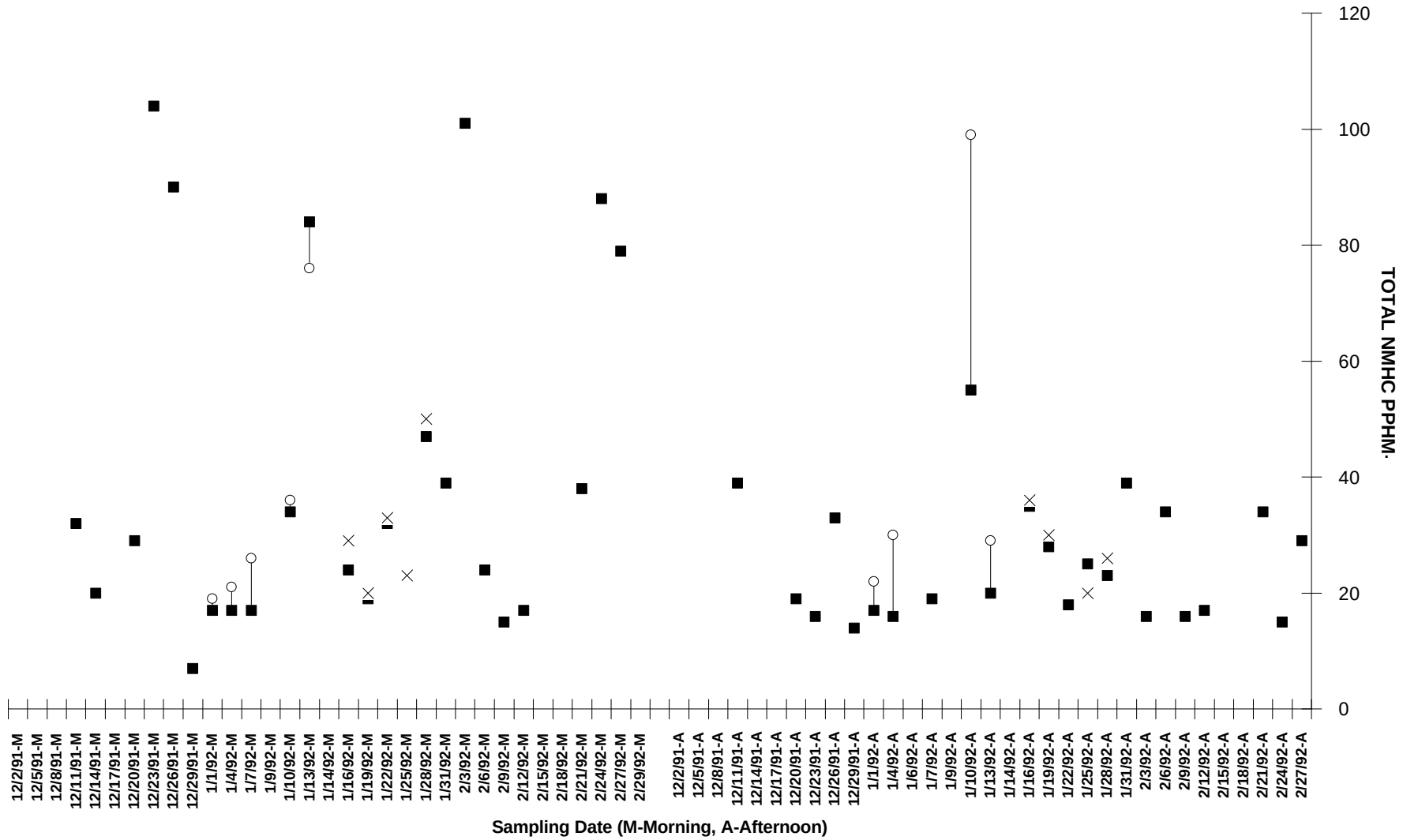


Figure 3. Total NMHC for All Sacramento Area Monitoring Sites (Winter 91-92)

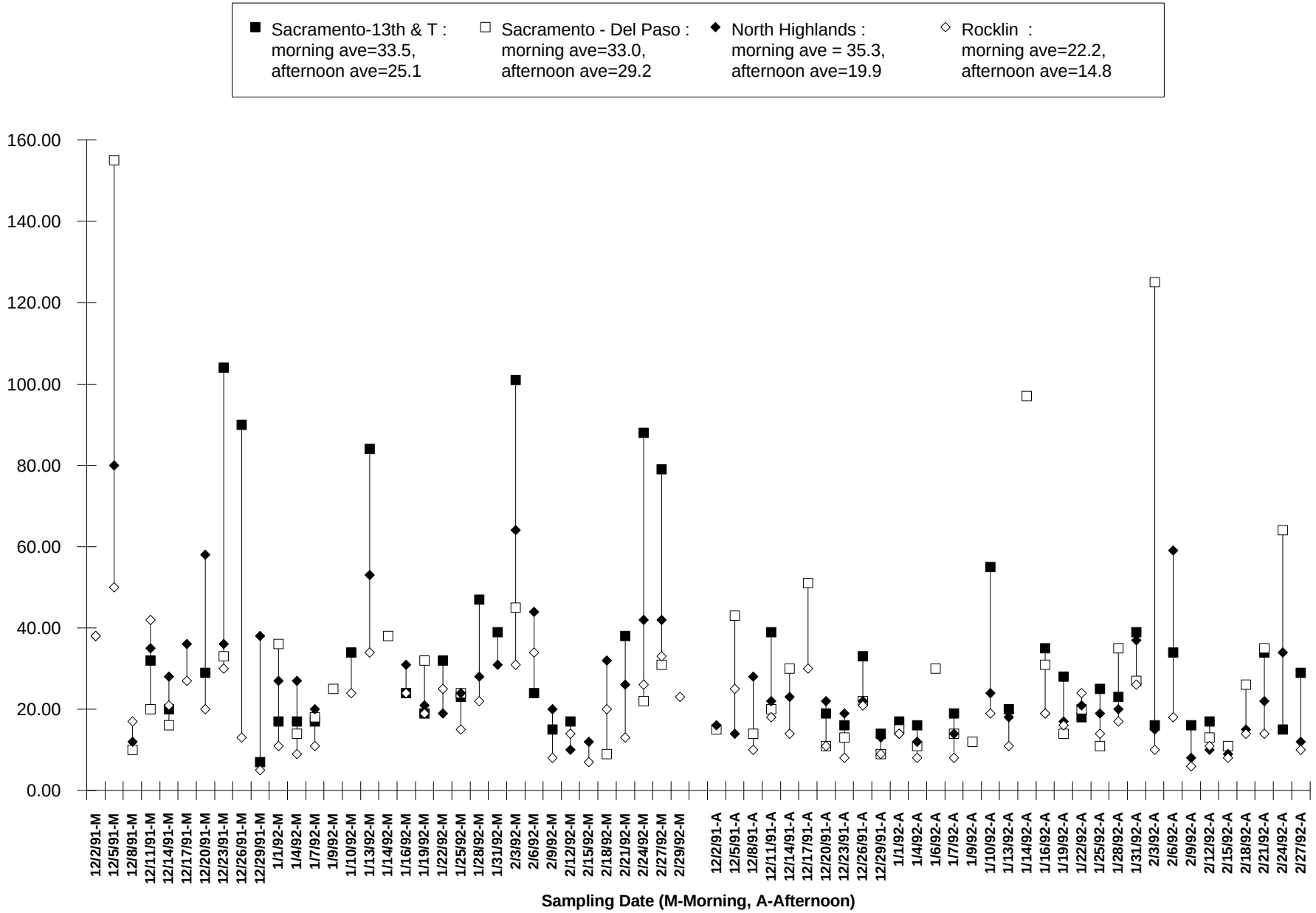


Figure 4. Sacramento (13th & T) Diurnal - Winter

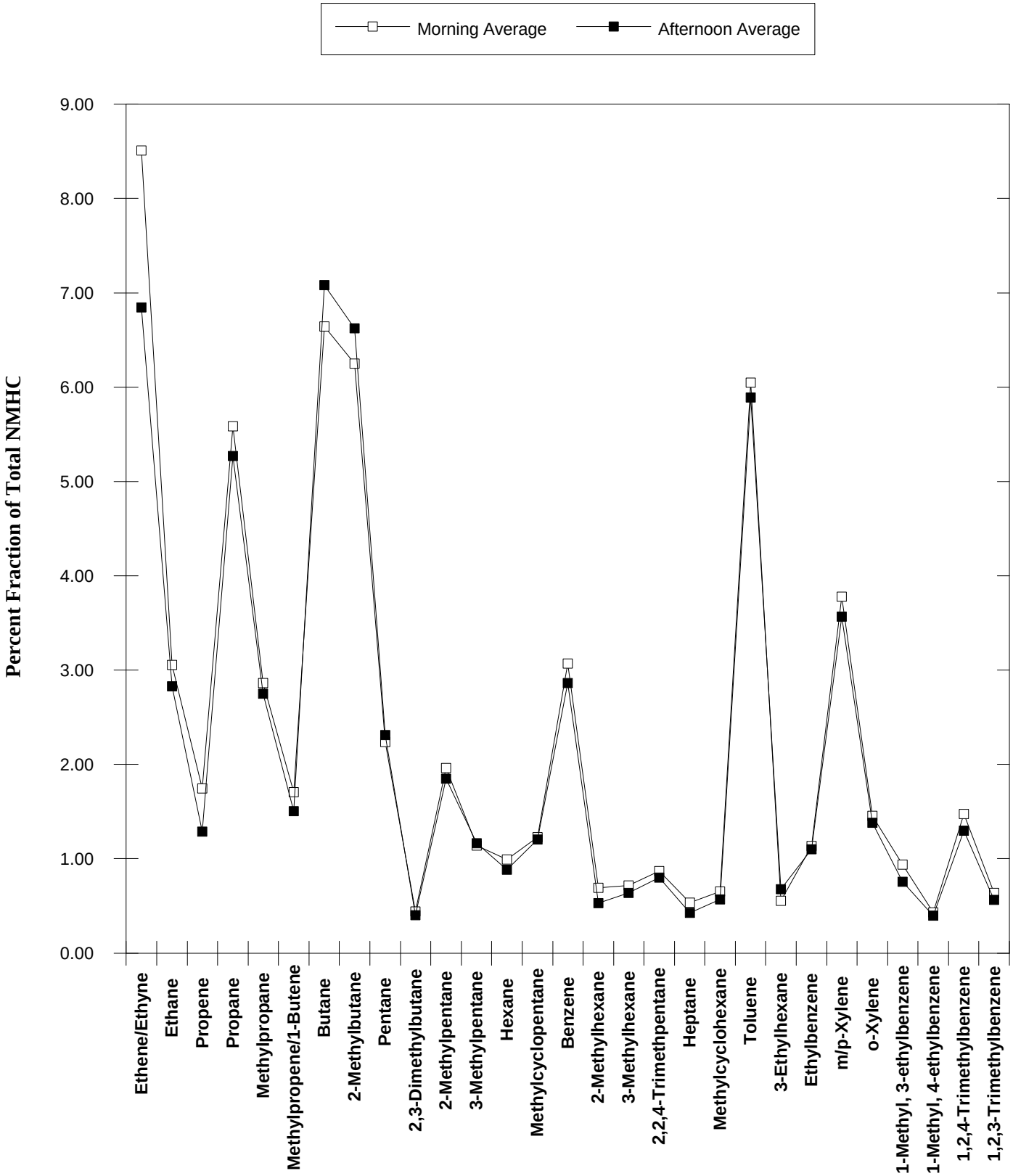


Figure 5. Sacramento (Del Paso) Diurnal - Winter

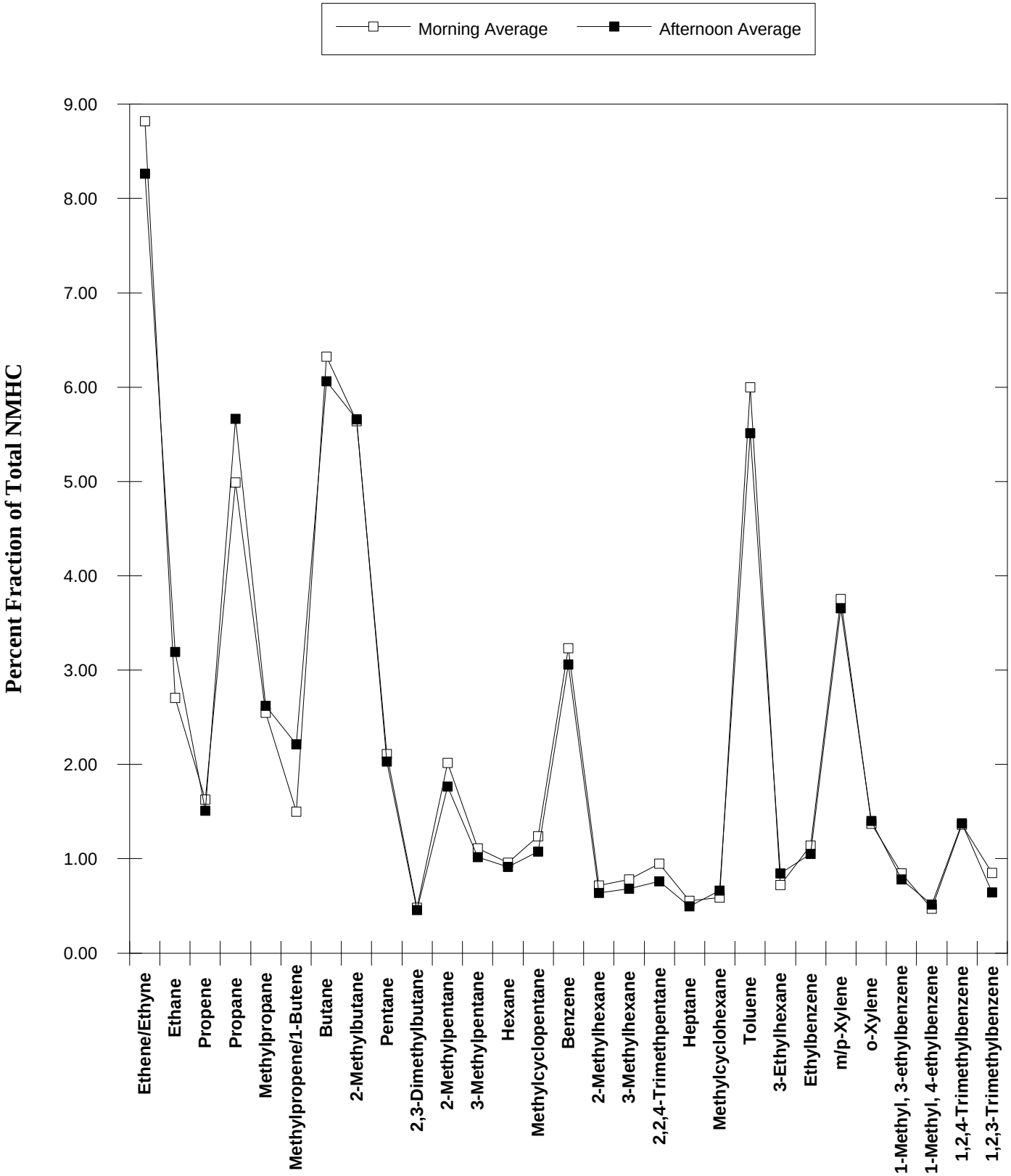


Figure 6. North Highlands Diurnal - Winter

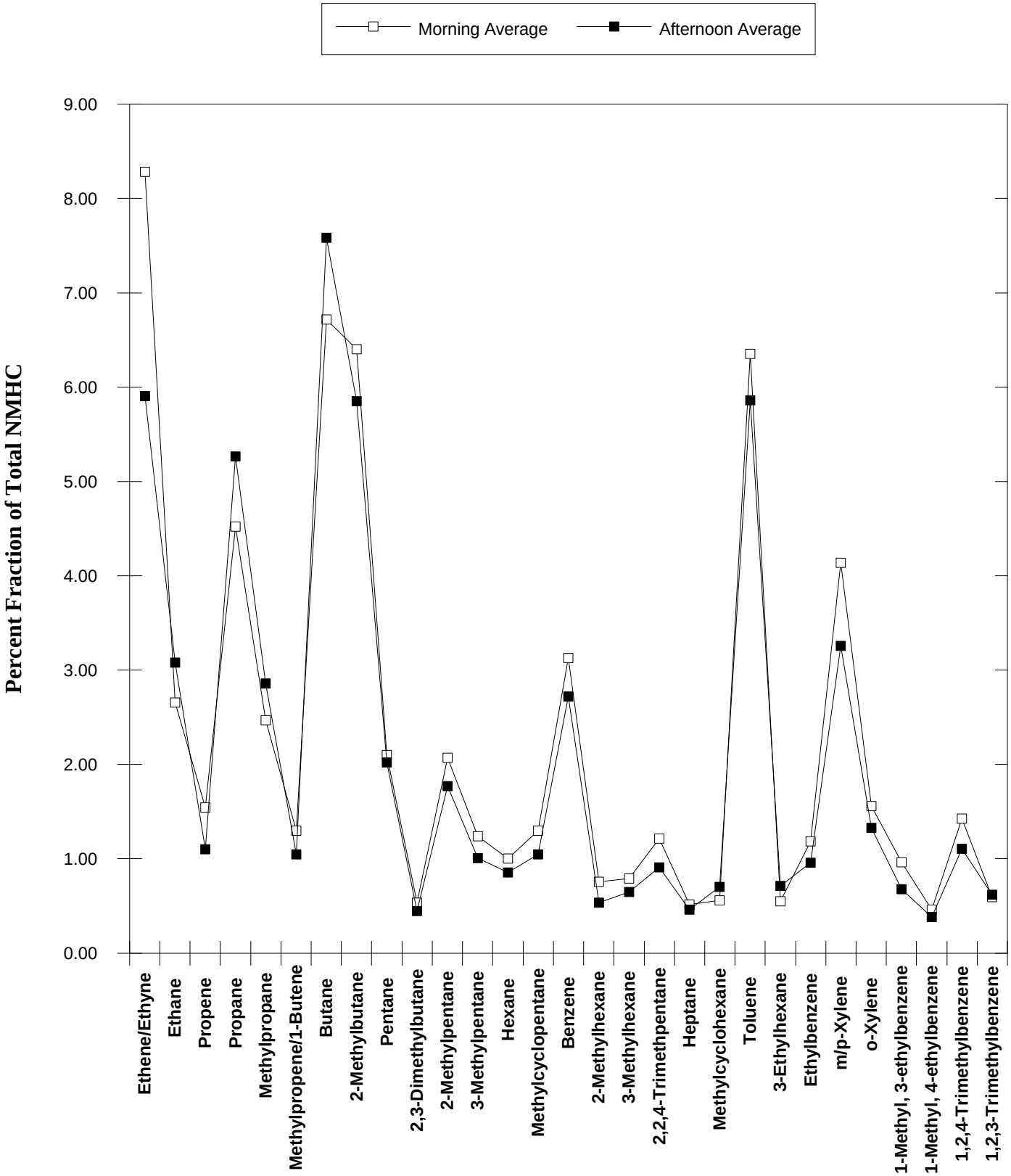


Figure 7. Rocklin Diurnal - Winter

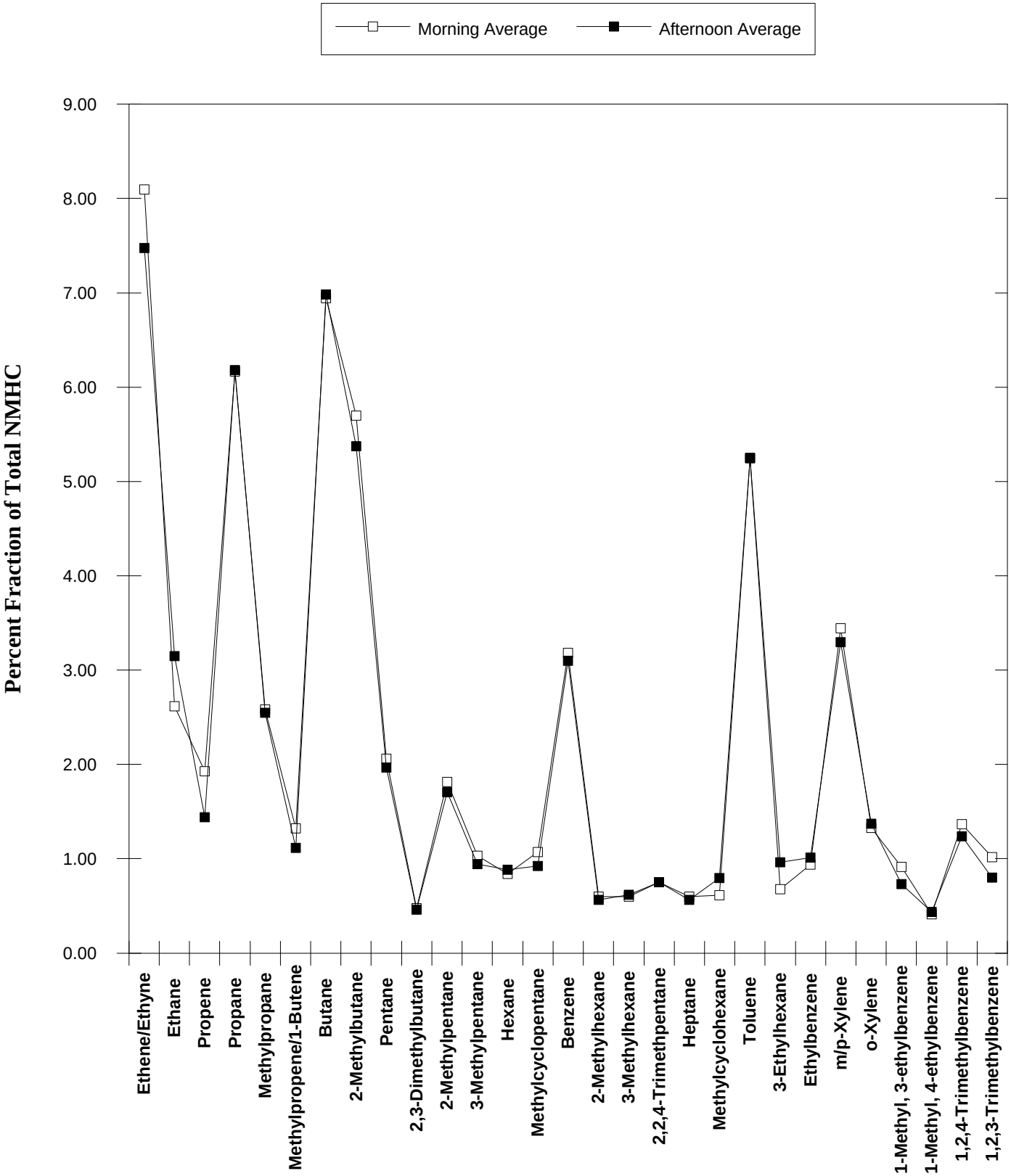


Figure 8. Sacramento - 13th & T
95% Confidence Interval of the Mean Percent Compound Fraction

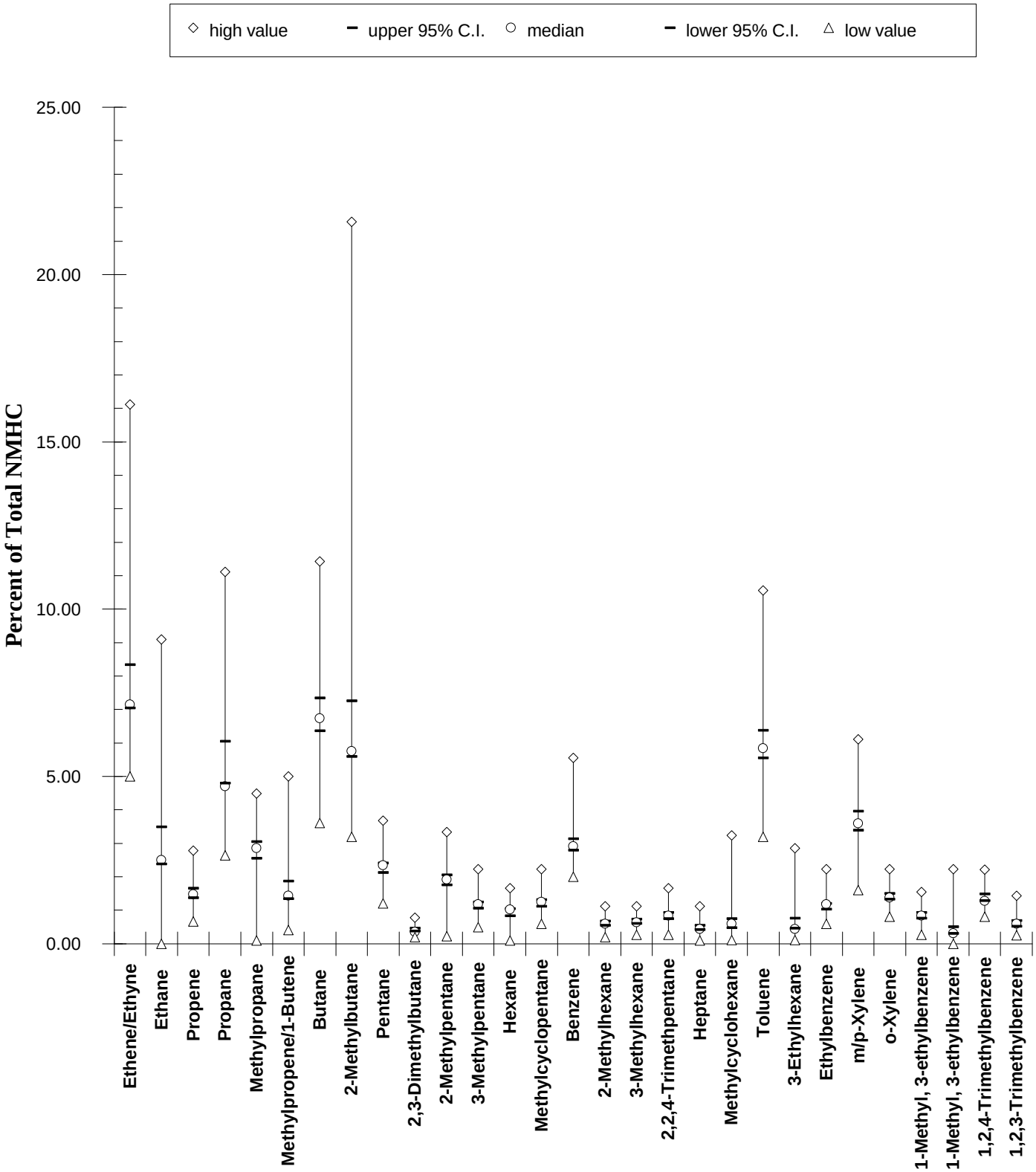


Figure 9. Sacramento (13th & T)

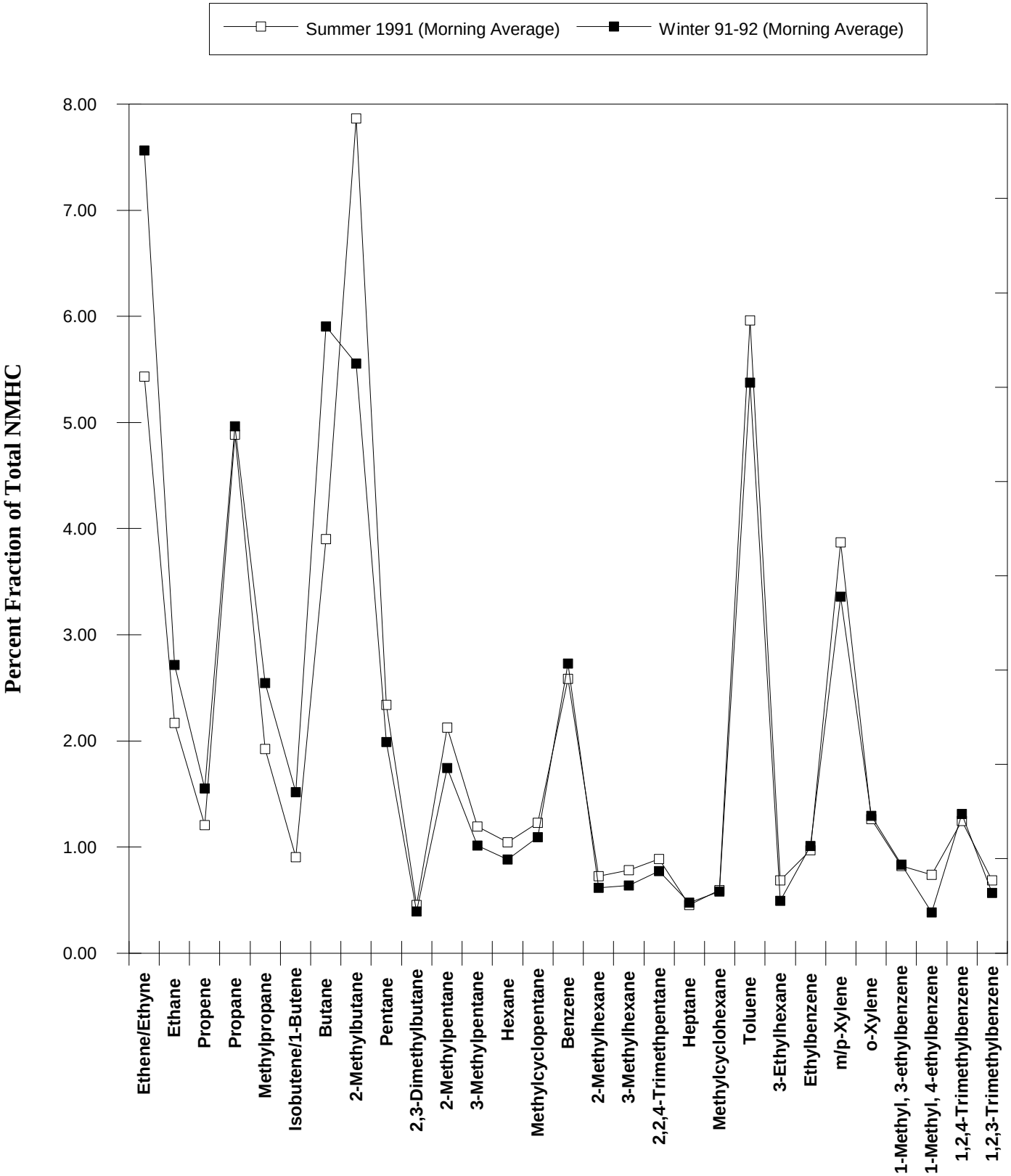


Figure 10. Average of the 7 Statewide Summer Sites for 1991
vs.
Average of 4 Sacramento Winter Sites of 1991-92